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Comparing the desorption of methanol to DME over ZSM-5 catalysts

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1. Introduction

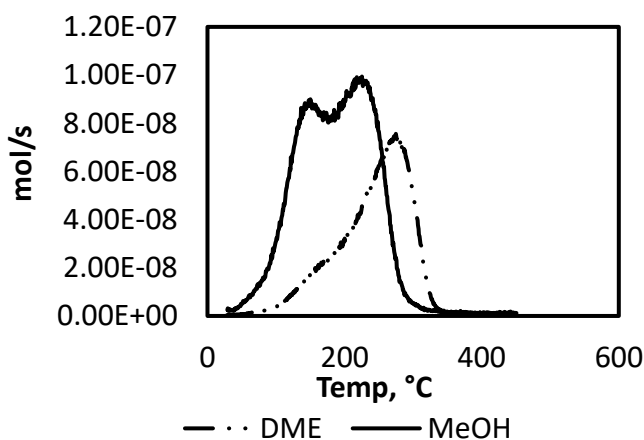
There exist three fundamental challenges on the conversion of methanol to hydrocarbons (MTH) over zeolite catalysts: (i) the identification of the primary reactant as methanol and its anhydrous equilibrium product, dimethyl ether (DME) initially compete for active sites, (ii) the validation of the first olefin formed and (iii) the dominating mechanism leading from the primary reactant to the first olefin. Direct mechanisms involving surface carbene, tri-methyloxonium ion, methyl ethyl ether, methane-formaldehyde, CO, and indirect mechanisms involving impurities (acetone or ethanol) have been suggested. These mechanisms lead to the pre-formation of a hydrocarbon pool which is responsible for steady state MTH conversion. This contribution investigates the primary reactant for MTH conversion.

2. Experimental

Fresh and activated ZSM-5 catalysts of different Si/Al ratios (25, 36 and 135) were used. The ammonium form of zeolites was pressed, crushed, and sieved to obtain particles sizes of 250 – 500 μm . Anhydrous DME (99.999%), Argon (99.999%) and ultra-high purity methanol (99.8%) were used. The protonated zeolite form was obtained by thermal treatment under vacuum, ramping at 15 $^{\circ}\text{C}/\text{min}$ to 450 $^{\circ}\text{C}$, holding for 30 min before being subsequently cooled at 25 $^{\circ}\text{C}/\text{min}$ to process temperature. Also, in separate experiments, the activated zeolite catalysts were obtained by subjecting the protonated zeolites to steady state MTH conversion at 370 $^{\circ}\text{C}$ and withdrawing after 2 hrs TOS. Temperature programmed desorption (TPD) experiments were conducted at different heating rates and initial coverages. Thereafter, desorption parameters were extracted separately using the Redhead and the Polanyi-Wigner method to account for the absence and presence of re-adsorption effects respectively.

3. Results and discussion

Using the redhead method, deconvolution of the desorption profile leads to identification of two desorption sites on ZSM-5 (25) and ZSM-5 (36) and three desorption sites on ZSM-5 (135). DME was observed to have a higher activation energy of desorption than methanol over fresh ZSM-5 catalysts. These sites were identified as low temperature Lewis sites and medium/high temperature Brønsted acid sites. In the absence of re-adsorption, the activation energies increase with Si/Al ratios. This effect is, however, removed when re-adsorption occurs in the pores. It was observed that the low temperature Lewis sites and medium temperature Brønsted acid sites are under equilibrium control. The high temperature Brønsted acid site was rationalised as oxygenate species migrating from the pore channel to the pore windows where they are in the equilibrium with the gas phase. The hydrocarbon pool and pore length largely control the activation energies of desorption over activated ZSM-5 samples.



4. Conclusions

This work identifies the key species involved in surface reactions as well as provides a detailed understanding on the diffusion of species in the zeolite pore structure. Also, the influence of the well-established hydrocarbon pool on the desorption of methanol and DME is elucidated.

ZSM-5 (25)